Electrophilic Addition Reaction of Ethene with Hydrogen Chloride on Cold Molecular Films: Evidence of Ethyl Cationic Intermediate

Poong-Ryul Lee, Chang-Woo Lee, Joon-Ki Kim, Eui-Seong Moon and Heon Kang

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Rabin Rajan J Methikkalam
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Trivalent carbocations are the intermediates in acid catalyzed electrophilic addition reaction of alkenes.

$\text{Carbocation}$

$1^\circ$ carbocations have neither been isolated nor identified with spectroscopy because of its lower thermodynamic stability and it was an experimental challenge of detecting $1^\circ$ carbocations.

Several studies demonstrated that a cold molecular surface can halt a reaction at an intermediate stage and the trapped intermediate can be identified with spectroscopic methods.
In the present work electrophilic addition reaction of ethene with HCl on frozen molecular films were carried out.

The study examines how the reaction proceeds on cold molecular surfaces and inspects the formation of ethyl cation intermediate (C$_2$H$_5^+$), the effect of water solvation and acid ionization on the reaction rate of the above reaction.

Temperature-programmed desorption (TPD), reactive ion scattering (RIS) and low-energy sputtering (LES) techniques were used for the study.
Experimental Section

- UHV chamber equipped with instrumentation for \( \text{Cs}^+ \) RIS, LES and TPD-MS.

- \( \text{D}_2\text{O} \) ice film was grown on a Ru(0001) substrate at 100 K and annealed at 140 K for 3 min to produce a polycrystalline ice film and the thickness was estimated by a TPD experiment as 2 bilayers (1BL = 1.1 \times 10^{15} \text{ water molecules cm}^{-2}).

- Ethene film was prepared by condensing \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{D}_4 \) at 73 K (1-2 molecular layers).

- \( \text{Cs}^+ \) beam from a low energy ion gun collided with the sample surface and the scattered ions were detected by a QMS with its ionizer filament switched off.
3.1. HCl and Ethene on water-ice film

Figure 1. TPD spectra of C$_2$H$_4$ adsorbed on D$_2$O-ice film (2 BL thickness) grown on Ru(0001). C$_2$H$_4$ gas exposure was 0.93 L (■) and 2.6 L (○). The sample heating rate was 1 K s$^{-1}$. The intensity scale is count s$^{-1}$.
Figure 2. LES and RIS signals measured from D$_2$O-ice film (2 BL thickness) with adsorbed C$_2$H$_4$ and HCl (Sample A). C$_2$H$_4$ and HCl gas exposures were 0.2 and 0.3 L, respectively. The spectrum was obtained at sample temperatures of 80 K (a) and 140 K (b). The signal intensities shown are reduced by the factors indicated.
Figure 3. TPD Spectra of C$_2$D$_4$ and HCl adsorbed on D$_2$O. Heating rate 1 K s$^{-1}$
3.2. Hydronium Ions and Ethene on water-ice film

Figure 4. LES and RIS signals from D₂O-ice film with adsorbed C₂H₄ and hydronium ions. Hydronium ions were generated from the ionization of HCl (0.3 L) on the ice surface at 140 K. C₂H₄ was then adsorbed on the surfaces at 73 K for 0.2 L. The spectrum was obtained at a sample temperature of 80 K.
3.3. Hydrogen Chloride on Frozen Ethene Film

Figure 5. LES and RIS results of Sample C, which was prepared by adsorbing 0.3 L of HCl onto C$_2$D$_4$ film condensed on Ru-(0001) at 73 K. The sample temperature was 80 K during acquisition of the spectra.
The adsorption of ethene and HCl on an ice surface leads to the formation of the $\pi$-complex of HCl and ethene which is stable below 93 K.

A small amount of ethyl cationic species is also formed on the surfaces below 100 K via direct proton transfer from molecular HCl to ethene and water solvation play a crucial role in this transfer.

At higher temperature the ethyl cation dissociates into ethene and hydronium and chloride ions.

Ethyl chloride is not formed because the passage over the reaction transition state is kinetically blocked on the ice surface.
- Organic reaction mechanism and its intermediates are more correctly predicted using RAIRS.
- Similar experiment can be done by producing H\(^+\) ions directly to the surfaces at low energy.
- Changing solvent will lead us to better understanding of the solvation phenomena in such reaction.
Thank you all...